Advanced Diagnostics of Ni-rich Layered Oxide Secondary Particles

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SLAC National Accelerator Laboratory

Annual Merit Review
DOE Vehicle Technologies Program
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BAT370

Overview

Timeline

- Project start date: December 2016
- Project end date: October 2021
- Percent complete: 30%

Barriers

- Barriers addressed
  - Advanced *in-situ* diagnostic to pinpoint and predict failures in batteries
  - Screen new battery chemistries using advanced diagnostic
  - Electrode lifetime

Budget

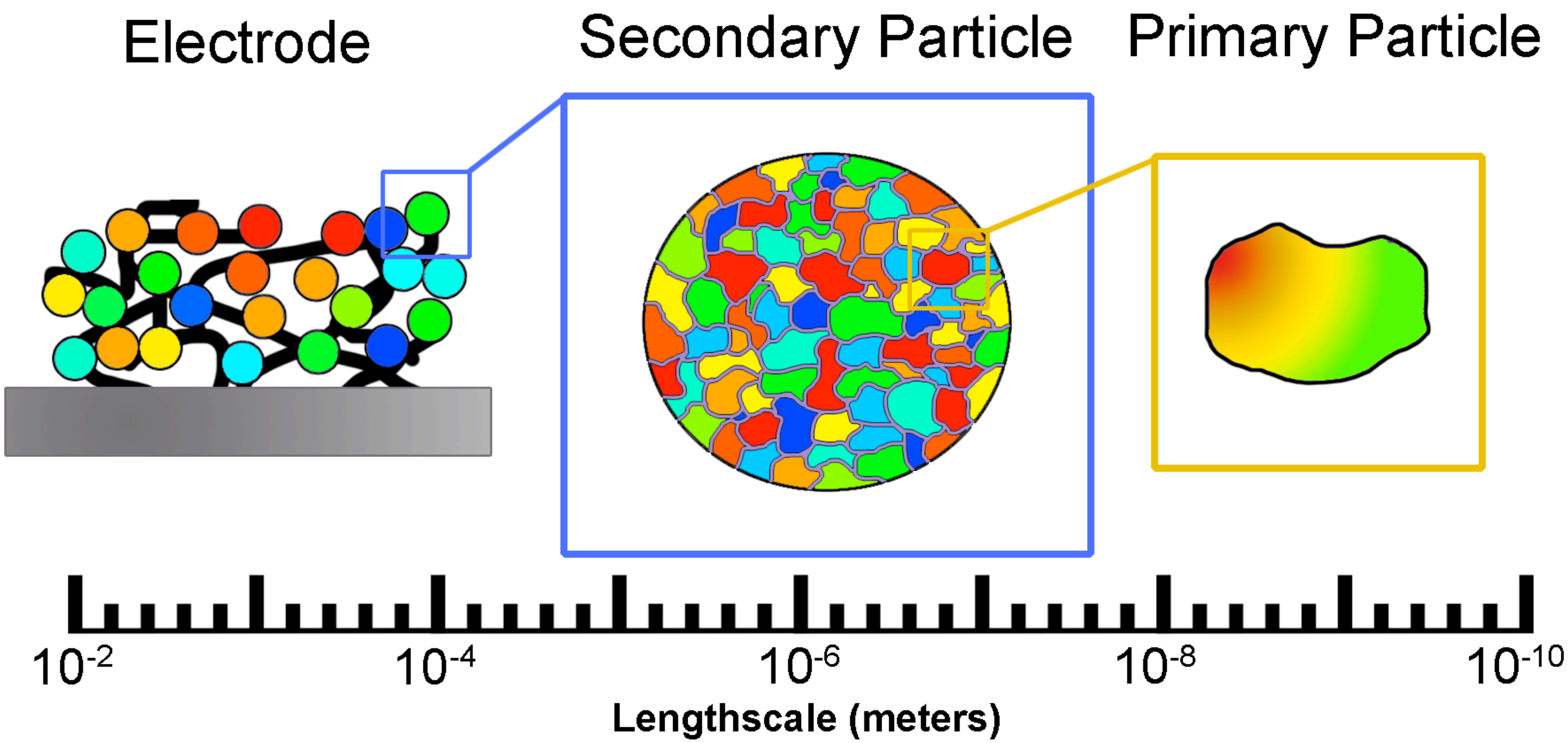
- Total project funding 50,000k
  - DOE share: 100%
- Funding for FY 2017:10,000k
- Funding for 2018: 10,000k

Partners

- PIs: Yi Cui, Will Chueh, Mike Toney
- Collaborators:
  - David Shapiro (Advanced Light Source)
  - Johanna Weker (Stanford Synchrotron Radiation Lightsource)

Objectives & Relevance

Objectives: Develop and utilize a correlative microscopy platform to investigate the coupling of electro-chemo-mechanical phenomena at all relevant length-scales for the specific goal of understanding factors that determine the rate capability and degradation mechanisms at the electrode, secondary particle, primary particle, and atomic length scales.



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Objectives & Relevance

Relevance:

- Understand atomistic and mesoscale factors that lead to capacity & voltage fading in layered oxide cathode materials (i.e. Ni-rich NMC)
- Develop diagnostic tools that reach new length scales not previously available

Impact:

- Enable accelerated materials development time by understanding capacity & voltage fade mechanisms
- Provide new information to design fast charging protocols and to improve power density
- Establish generalized characterization and analysis platform for advanced energy storage materials characterization

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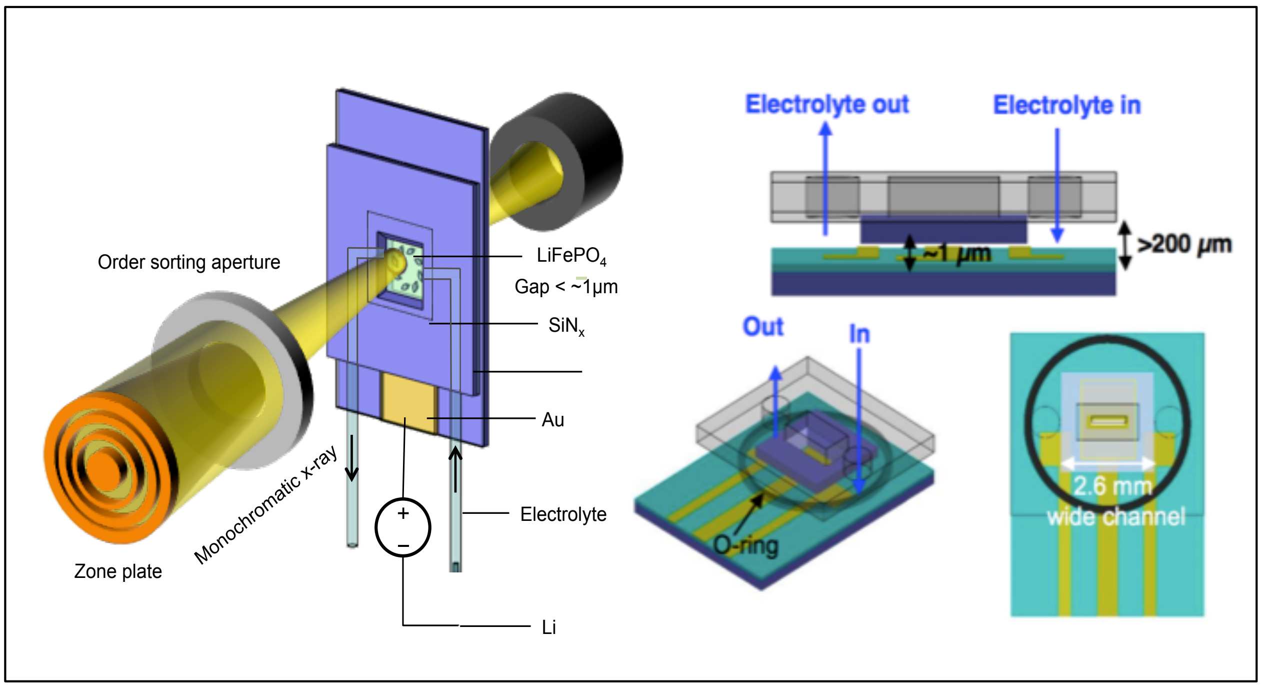
Milestones

- Design and construct in situ XRD cells for depth –profile studies of thick high Ni cathode materials (12/31/2017, complete)
- Complete the set-up of in-situ characterization of full cells (3/31/2018, complete)
- Develop procedures to identify Li metal anode failure in coin cells (6/30/2018, on track)
- Establish the proper imaging and diagnosis of Li metal anode with different electrolytes and electrolytes additives (9/31/2018, on track)

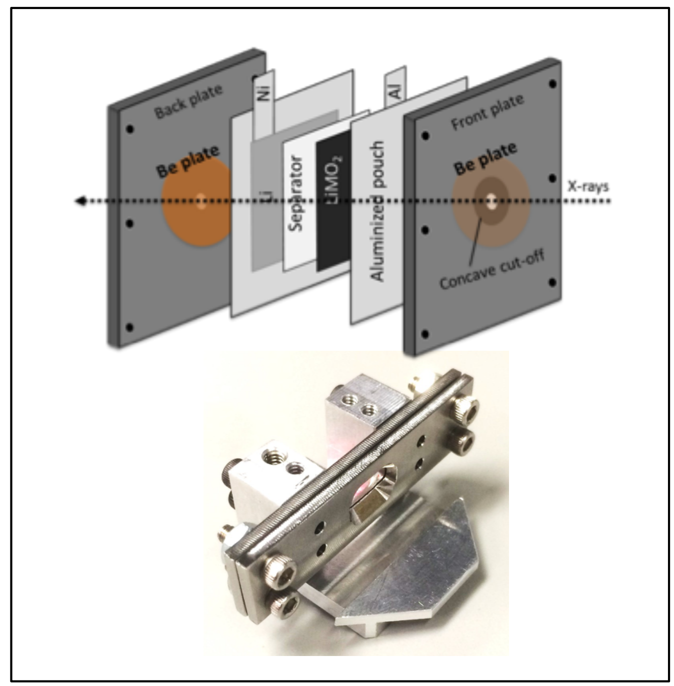
Approach

- Develop & utilize in-situ & ex-situ X-ray spectro-microscopy to relate local chemistry and microstructure evolution to battery electrochemical characteristics (voltage, capacity/voltage fade, and activation).
- Develop advanced data/image analysis techniques
- Correlate with other characterizations such as diffraction & electron microscopy.

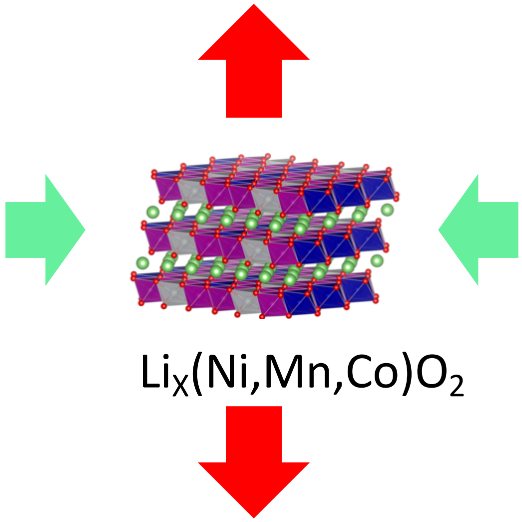
Soft X-ray Transmission (< 300 nm penetration)



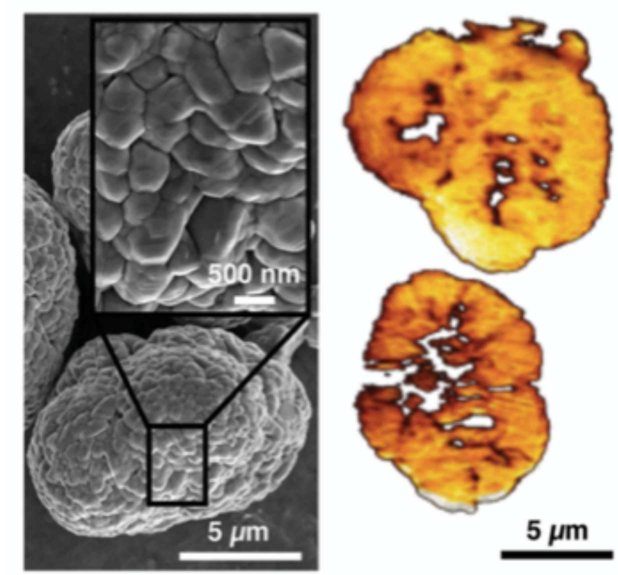
Hard X-ray Transmission (< 50 μm penetration)



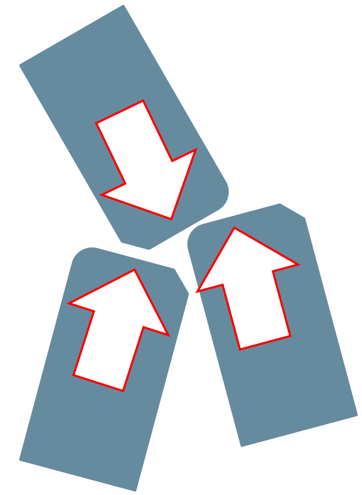
Technical Progress: Connecting Phase, Microstructure and Electrochemical Heterogeneity in Ni-Rich NMC



Single primary particle

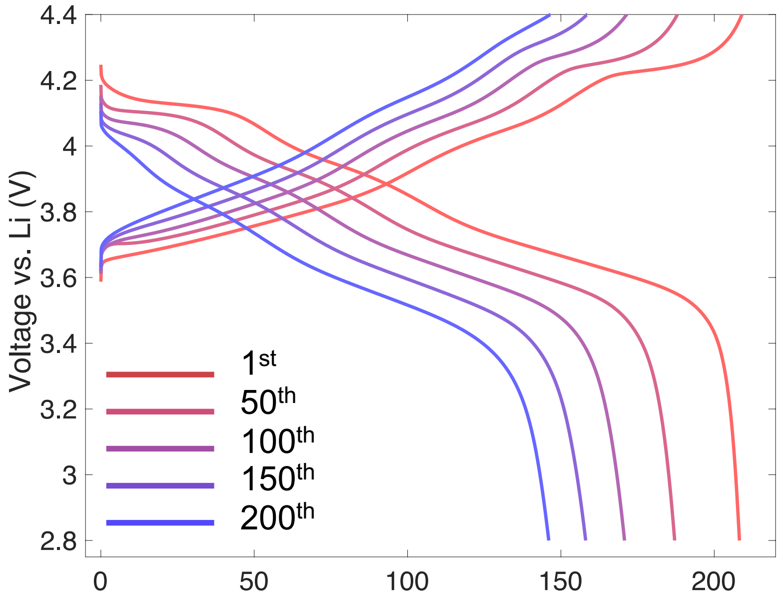


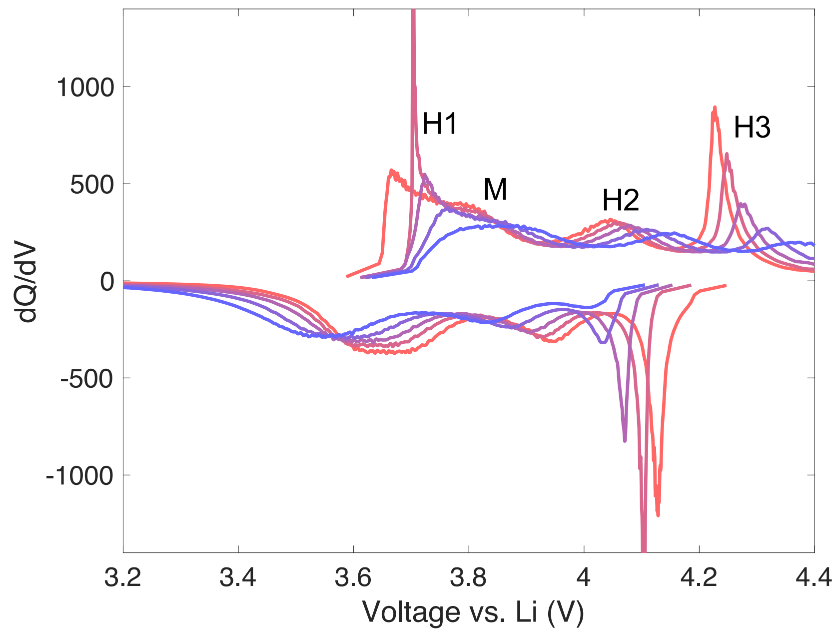
Secondary particle

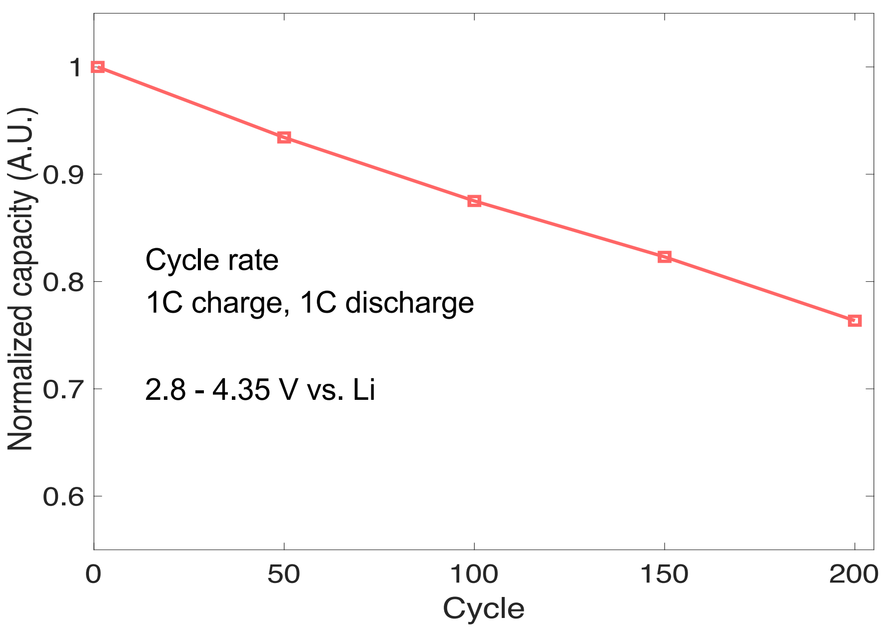


- All layered oxides and graphite exhibit anisotropic chemical expansion upon lithium insertion.
- Preferred orientation in the secondary particle during co-precipitation synthesis of layered oxides give rise stress concentration points throughout the secondary particles, resulting in non-uniform strain.

Rapid capacity fade in Ni-rich NMC is coupled to chemo-mechanics through phase-change

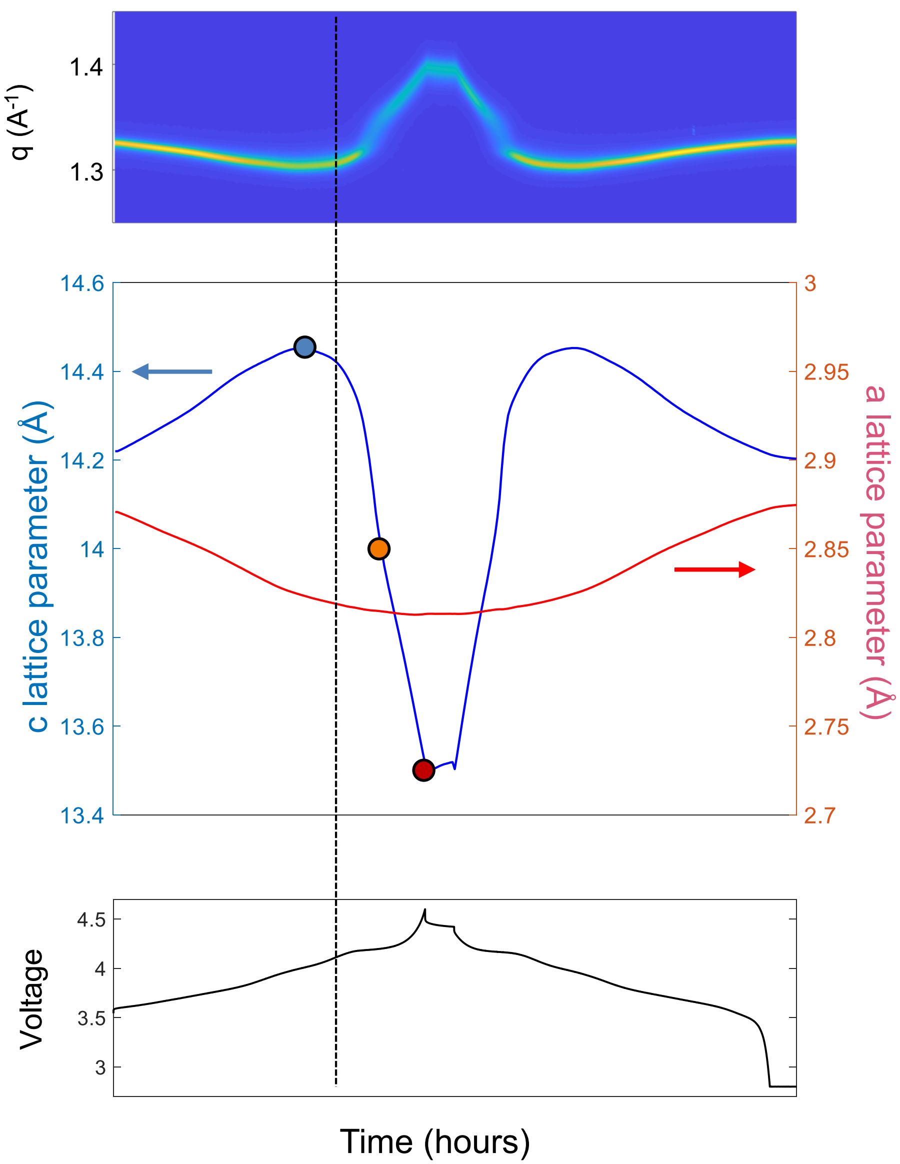


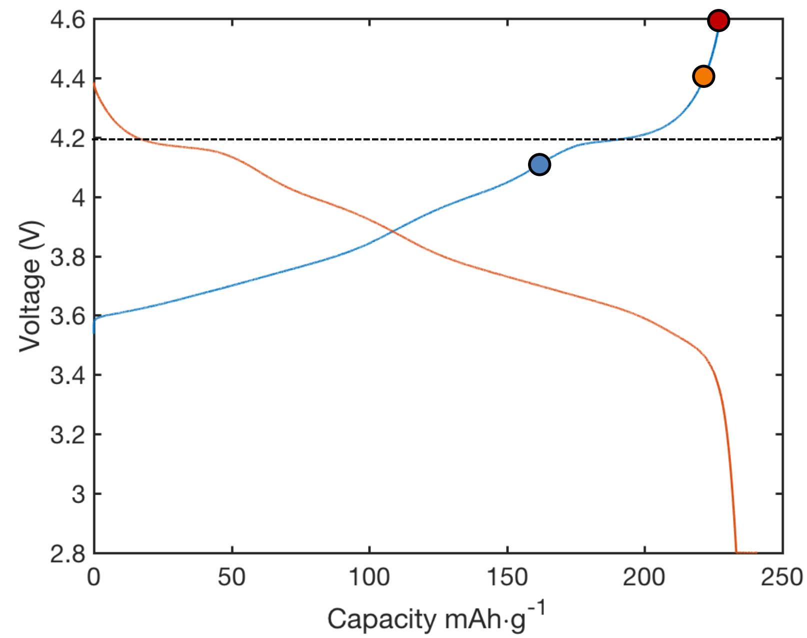




- Fast capacity fade observed over 200 cycles
- Differential capacity data shows phase behavior/voltage onset shifts significantly with cycling

Anisotropic chemical expansion





- Operando XRD shows rapid collapse of c-lattice >~4.2V, corresponding to large chemical strain
- Reversal in inter-slab distance is reversible but correlated with faster capacity fade

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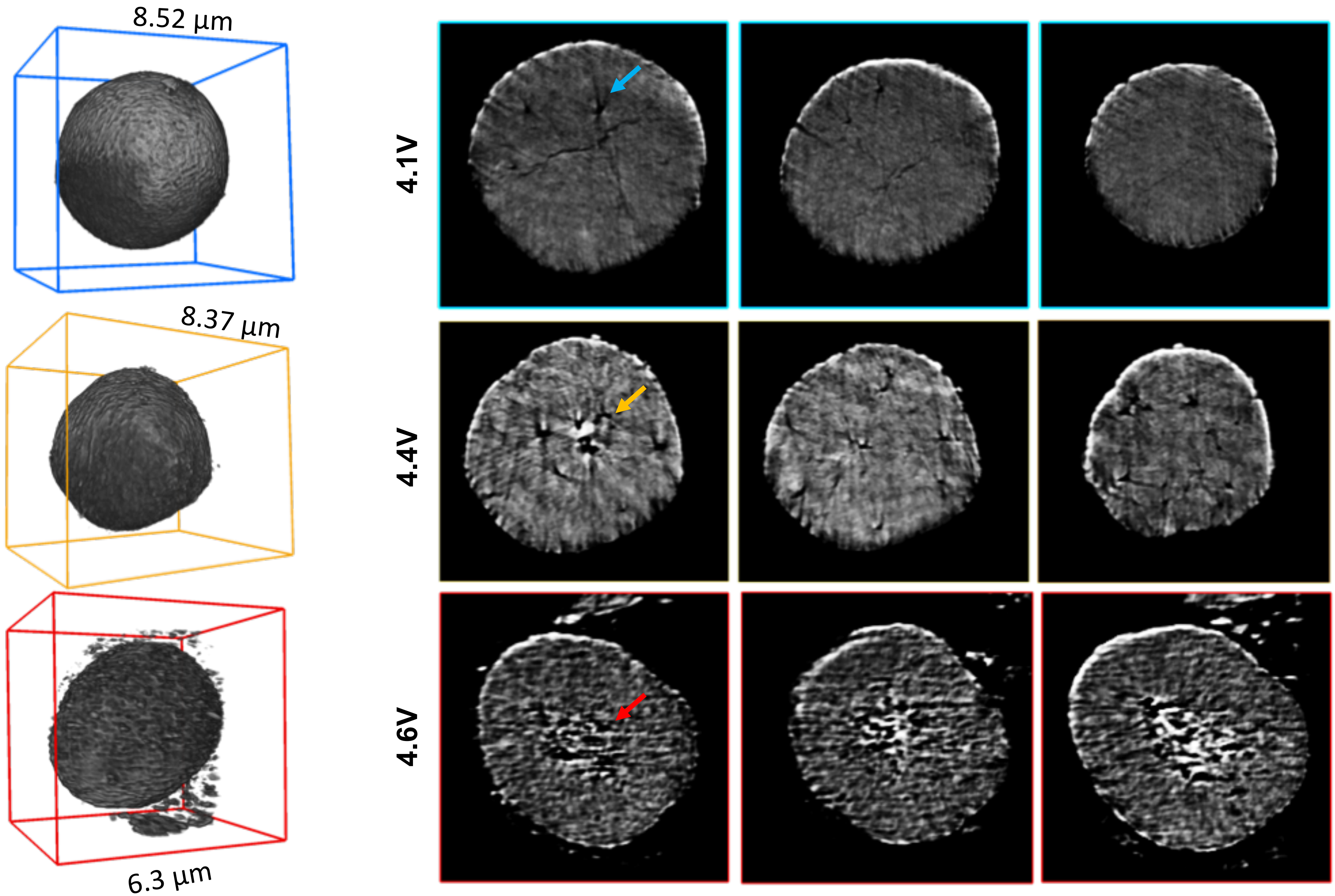
Microstructure evolution after 1st cycle charging



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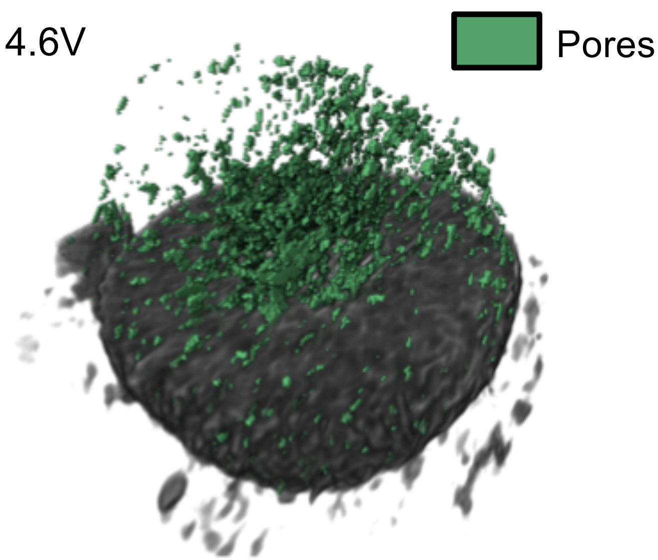

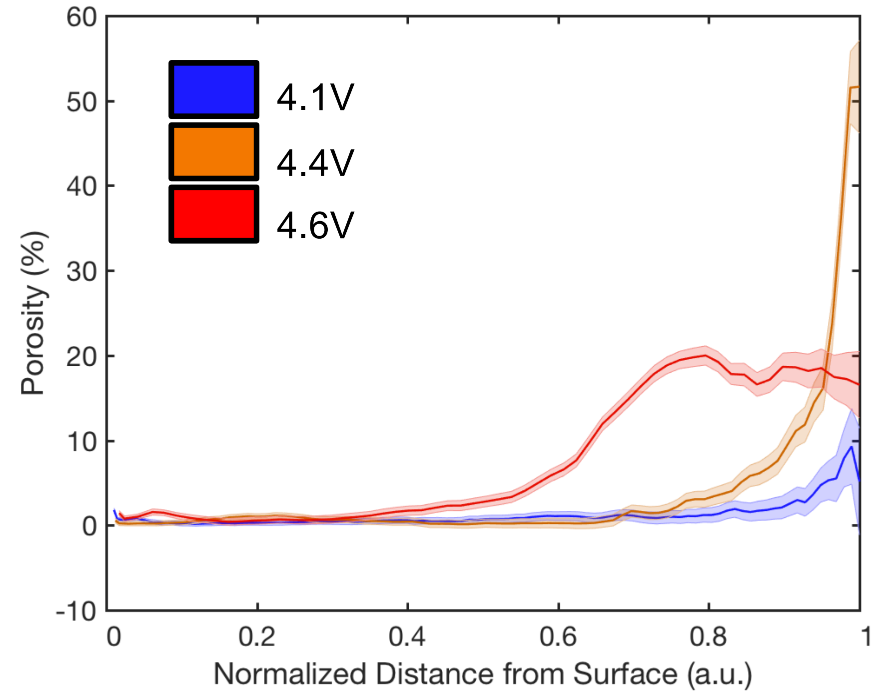

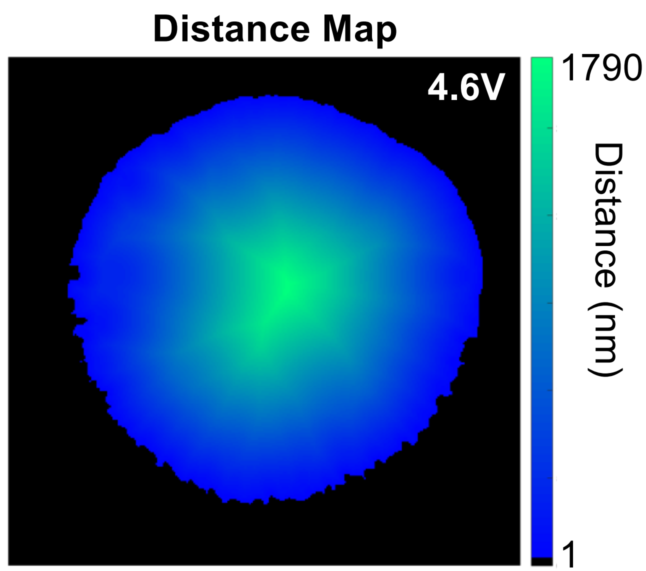

- Segmentation of the particle and pore space was performed for each particle.
- Formation and propagation of cracks occur inside-out. Very little crack formation on particle exterior (at our mesoscale resolutions).

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Response to Previous Year Reviewer's Comments

None

Collaboration & Coordination with Other Institutions

Advanced Light Source, LBNL:

- Users facility accessed via proposal (no cost)
- Carry out X-ray microscopy experiments at beam line 11.0.2, 5.3.2

Stanford Synchrotron Radiation Lightsource

- Users facility accessed via proposal (no cost)
- Carry out X-ray tomography

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Remaining Challenges & Barriers

- Translate ex-situ experiment to in-situ for both secondary & primary particles
- Phase transformation in NMC has a very weak spectroscopic signature
- Couple nanoscale mapping to nanoscale crystallography in full cells

Proposed Future Research

- Apply to various Ni-rich compositions investigated by Battery500 to correlate capacity fade to microstructure and chemical changes at the electrode, secondary and primary particle levels.
- Quantification cathode/electrolyte interphase chemistry using spectro-microscopy, and its sensitivity to the location in the porous electrode.
- Quantification of dead Li.

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Summary

- Developed 3-D transmission X-ray microscopy to characterize the evolution of internal pore structure and cracking in Ni-rich NMC as a function of voltage and cycling.
- The induced stresses and accompanying SOC heterogeneity have detrimental effect on the material cycle life by accelerating secondary particle fracture and resulting in locally overcharged domains at the cutoff voltage, which was revealed by X-ray microscopy.
- Developed dry sectioning technique to prepare electron and X-ray transparent cross sections of Ni-rich NMC cathodes while retaining complete electrode microstructure.

Acknowledgement

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